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Alkylative Dearomatization by Using an Unactivated Aryl Nitro Group as a Leaving Group: Access to Diversified Alkylated Spiro[5.5]trienones

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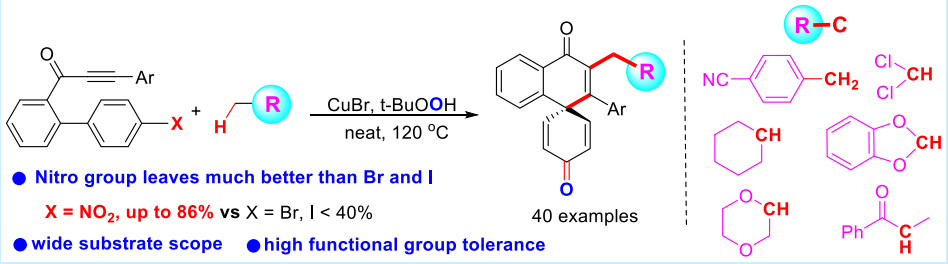


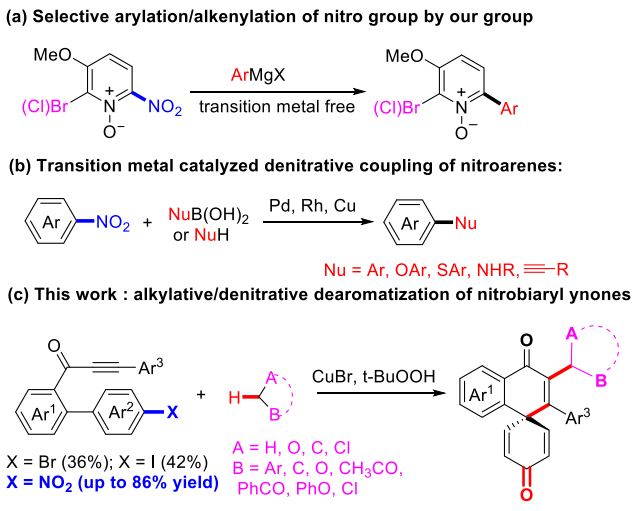
ABSTRACT: The cleavage of an unactivated aryl nitro group triggered by alkyl radicals enables a dearomative cyclization, affording diversified alkylated spiro[5.5]trienones in good yields. Using readily available compounds (toluene and analogues, alkanes, ethers, ketones, etc.) as alkylating reagents, various alkyls have been implanted into the spirocycles via C(sp^3)−H and Ar−NO_2 bond activation with high functional group tolerance. This protocol provides a distinct method for the activation of the aryl nitro group.

Nitroarenes are very common and versatile compounds in organic synthesis that can be conveniently prepared by nitration of the parent arenes. Through reduction and subsequent diazotization, they are the starting point for many important building blocks such as anilines, aryl halides, phenols, and so on.[1] Aryl halides and phenol-derived esters (sulfonates, carbamates, sulfamates, etc.) are the most commonly used electrophiles for transition-metal-catalyzed coupling reactions in constructing C−C and C−X bonds.[2] In this context, the direct use of nitroarenes as an electrophile in coupling reactions, which can avoid the multistep conversions to access halides and phenol esters, is a challenging yet step-economic task.[3]

We have previously reported an efficient arylation reaction of nitropyridine N-oxides in which the nitro group served as a better leaving group than the well-known Br and Cl groups (Scheme 1a).[4] Nevertheless, that direct substitution of the nitro group was limited to activated nitros.[1,4,5] On the contrary, Wu, Shinde, Nakao, You, and coworkers reported various Pd-, Rh-, and Cu-catalyzed direct couplings of activated and unactivated nitroarenes to form C−C and C−X bonds (Scheme 1b).[6−9] Despite these achievements, an alkylative and alkenylative reaction using an unactivated aryl nitro group as a leaving group remains quite elusive. In addition, the selective substitution of a nitro group over Br or Cl has not been documented in these transition-metal-catalyzed reactions.

We herein report an alkylative dearomatization enabled by the cleavage of an unactivated aryl nitro group (Scheme 1c). Interestingly, in this dearomatization, the nitro group served as a much better leaving group than the classic Br and I, which provides an alternative method for the activation of the aryl

Scheme 1. Denitrative Reactions of Nitroarenes



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nitro group. We expect that these findings will provide implications for the activation of aryl nitro group and related reactions.

On the basis of our continued interest in the cleavage of unactivated Ar−NO_2 bonds, we hypothesized that a radical-type alkylation or alkenylation might provide a distinct method for the activation of the aryl nitro group.[10] Meanwhile, spiro[5.5]trienones are important structural motifs because such cores and their analogues are often found in natural products and bioactive compounds (Figure 1).[11] We assumed

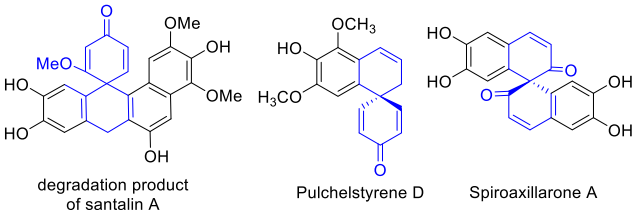
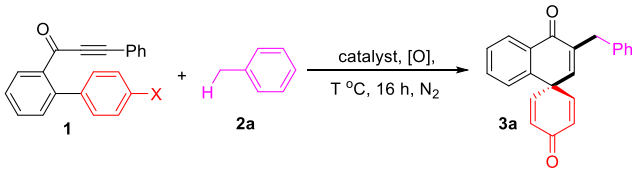


Figure 1. Natural products with spiro[5.5]trienone core.

that a radical alkylation of the nitrobiaryl ynone (**1a**: X = NO_2) might promote the leaving of a nitro group and a dearomative cyclization to the desired spiro[5.5]enone core in a tandem reaction manner.[12−14] Thus we started our investigation with the mode reaction between **1** and toluene, and the results are outlined in Table 1. It can be seen that the leaving group (X), catalyst, oxidant, reaction temperature, and solvent had a significant influence on the outcome of the reaction. Under optimized conditions (entry 1), the nitro group turned out to be the best leaving group, whereas the classic good leaving groups Br and I resulted in only low yields (entries 1−5). It is noteworthy that all of the reported dearomative cyclizations of biaryl ynone to spiro[5.5]trienones have relied on MeO to form C═O by demethylation in the Ar^2 ring (X = OMe; shown in Scheme 1c).[12] Instead, our protocol provided a new strategy via a nitro cleavage and afforded an even better yield (entry 1 vs 3). Ordinarily, alkyl halides are used as radical precursors, whereas the present reaction used only simple toluene, representing a C(sp^3)−H activation. The screening of temperature (entries 6−8), Cu source (entries 10−14), and oxidants (entries 16−22 and 25) indicated that the present reaction proceeded optimally with 5 mol % CuBr and 4 equiv of TBHP at 120 °C. It should be mentioned that this mode reaction also occurred without a catalyst in a 77% yield (entry 9); nevertheless, other substrates gave rather low yields during our later exploration of the substrate scope. We hypothesize that Cu(I)/(II) plays a catalytic role by promoting the generation of free radicals such as *t*-BuOO· and *t*-BuO·. (For details, see Scheme 5.) Solvent optimization showed that toluene can efficiently serve as both the reactant and the solvent without the need for other solvents (entries 23 and 24), which made the reaction composition simpler.

With the optimized conditions in hand, we investigated the substrate scope with the initial focus on the reaction of the aromatic methyl groups of toluene and analogues. Although the benzylic C(sp^3)−H bonds performed efficiently in a range of radical reactions,[15,16] their propensity to form alcohols, aldehydes, acids, or nitrile in the presence of the oxidants presents a significant challenge to our desired reaction.[17] Despite this challenge, our results outlined in Scheme 2 show that the benzylative/denitrative dearomatization proved to be robust and general. Various chloro- or bromotoluenes can

Table 1. Optimization of Reaction Conditions[a]



entry	X	catalyst	oxidant	*T* (°C)	yield (%)[b]
1	NO_2 (**1a**)	CuBr	TBHP[c]	120	86
2	H (1b)	CuBr	TBHP	120	28
3	OMe (**1c**)	CuBr	TBHP	120	73
4	Br (**1d**)	CuBr	TBHP	120	38
5	I (**1e**)	CuBr	TBHP	120	40
6	**1a**	CuBr	TBHP	80	trace
7	**1a**	CuBr	TBHP	100	65
8	**1a**	CuBr	TBHP	130	84
9	**1a**		TBHP	120	77
10	**1a**	CuCl	TBHP	120	81
11	**1a**	CuI	TBHP	120	78
12	**1a**	Cu	TBHP	120	77
13	**1a**	CuO	TBHP	120	80
14	**1a**	$Cu(OAc)_2$	TBHP	120	78
15	**1a**	CuBr		120	trace
16	**1a**	CuBr	DCP[d]	120	76
17	**1a**	CuBr	DTBP[e]	120	73
18	**1a**	CuBr	CHP[f]	120	64
19	**1a**	CuBr	TBPB[g]	120	56
20	**1a**	CuBr	H_2O_2[h]	120	45
21	**1a**	CuBr	$K_2S_2O_8$	120	13
22	**1a**	CuBr	$(NH_4)S_2O_8$	120	11
23[i]	**1a**	CuBr	TBHP	120	34
24[j]	**1a**	CuBr	TBHP	120	40
25[k]	**1a**	CuBr	TBHP	120	70

[a]Unless otherwise noted, the reactions were carried out with **1** (0.25 mmol), **2a** (2 mL), oxidant (1.0 mmol), and 5 mol % of catalyst for 16 h under a N_2 atmosphere. [b]Isolated yield. [c]TBHP, *t*-BuOOH (70% aq). [d]DCP, dicumyl peroxide. [e]DTBP, di-*tert*-butyl peroxide. [f]CHP, cumene hydroperoxide. [g]TBPB, *tert*-butyl peroxybenzoate. [h]30% aq. [i]In a mixture of toluene and THF (1/1 v/v, 2 mL). [j]In a mixture of toluene and DMF (1/1 v/v, 2 mL). [k]TBHP was used in 0.75 mmol.

undergo the reaction with no debromination or dechlorination being observed (**3b−3f**). Xylenes and mesitylene can both afford the desired monobenzylated products in high yields (**3g−3j**). The reaction also showed a high functional group tolerance: CN and $COCH_3$, which were usually sensitive to strong oxidants, remained untouched under the present conditions (**3k** and **3l**). It should be noted that the benzylic C(sp^3)−H demonstrated a high selectivity over the methyl group of $COCH_3$ (**3l**) and OCH_3 (**3m**), although these methyls are also susceptible to the radical reactions. (Also see Scheme 3.)[15] The high selectivity between the different methyl groups of **1** and **2** was also achieved, in which the methyl on the Ar^1 ring (shown in Scheme 1c) remained untouched (**3n** and **3o**). Likewise, the Me, Et, *t*-Bu, and OMe groups on the Ar^3 ring (tethered to the alkyne, shown in Scheme 1c) (**3t−3w**), whose benzylic C(sp^3)−H or C(sp^3)−H in the methyl group can also produce radicals under the present conditions, did not interfere with the present benzylation. Regretfully, the benzylations using ethylbenzene, isopropylbenzene and their analogues failed in our hands. Although a similar effect was

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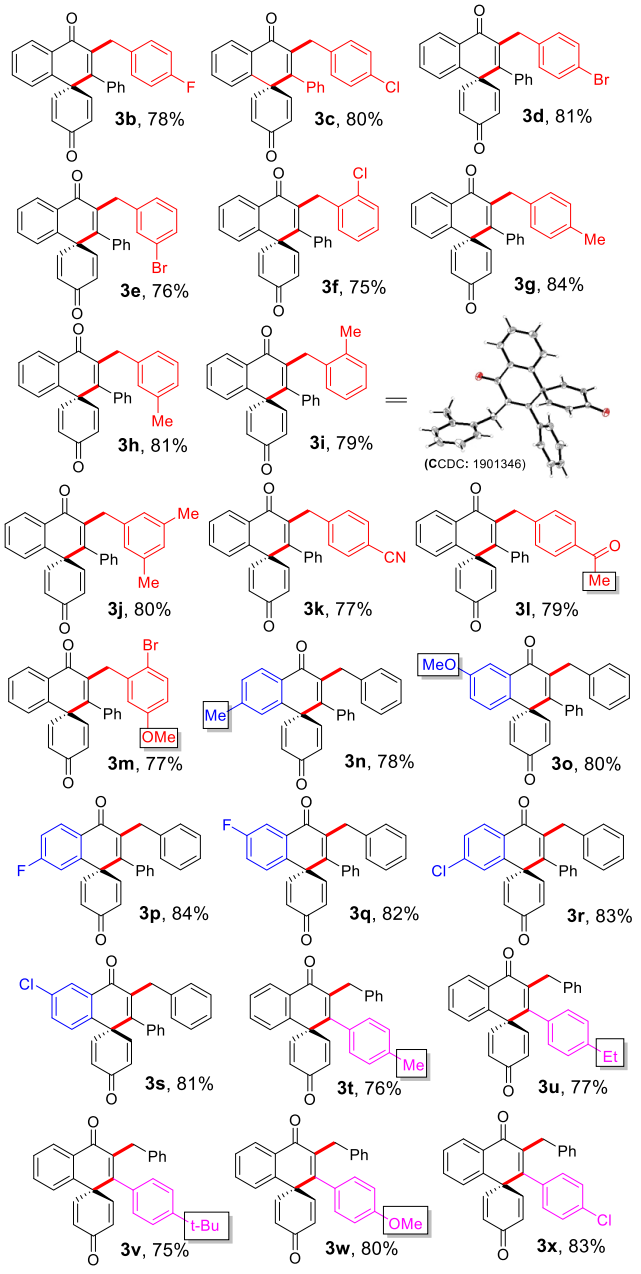
Scheme 2. Benzylative/Denitrative Dearomatizations to Spiro[5.5]trienones Using Toluene Derivatives[a]

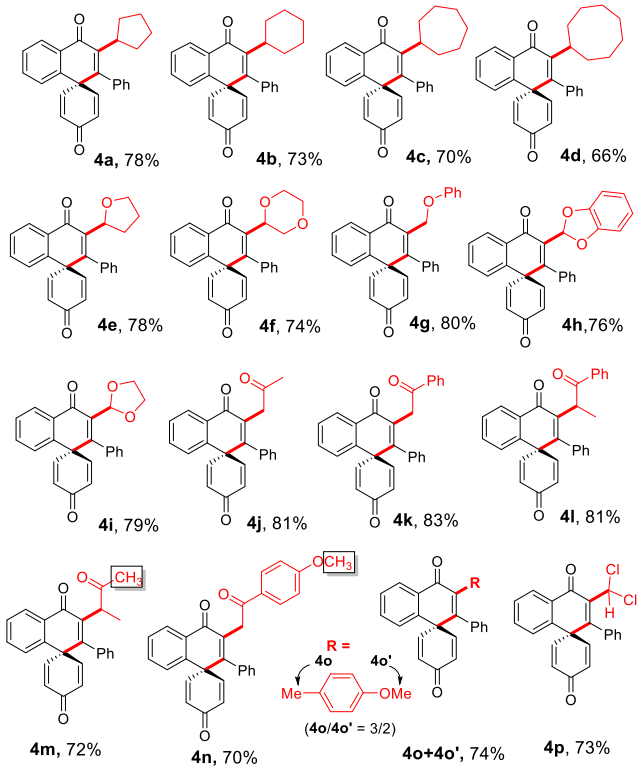


[a]Reaction conditions: **1** (0.25 mmol), **2** (2 mL), CuBr (5 mol %), TBHP (4.0 equiv), 120 °C, 16 h, N_2.

reported in a radical cyclization,[18] other reasons besides steric hindrance remain to be discovered.

Next, we explored the alkylative dearomatization using alkanes, ethers, ketones, and so on (in Scheme 3). The previously mentioned failure of the alkylation *via* secondary benzyl C−H bonds makes us think that the alkylation using secondary or tertiary alkylating reagents may be challenging. Despite this fact, the alkylative spirocyclization using unactivated cycloalkanes[15,19] occurred smoothly (**4a**−**4d**). Common ether solvents (THF, 1,4-dioxane) and anisole can also participate in the alkylation (**4e**−**4g**).[15,20] Acetals can undergo the present reaction in the presence of oxidants and water (**4h** and **4i**), demonstrating the wide scope and good functional compatibility. Although aromatic methyl group(s)

Scheme 3. Alkylative/Denitrative Dearomatizations to Spiro[5.5]trienones Using Alkanes, Ethers, and Ketones[a]



[a]Reaction conditions: **1a** (0.25 mmol), **2** (2 mL), CuBr (5 mol %), TBHP (4.0 equiv), 120 °C, 16 h, N_2.

reacted preferentially to the α-CH_3 group of ketones (**3l** in Scheme 2), the α-CH_3 or CH_2 groups of ketones underwent the spirocyclization facilely in the absence of aromatic methyl group(s) in high yields (**4j**−**4n**). It can be seen that the α-CH_2 group of ketone reacted highly selectively over the α-CH_3 group (**4m**), whereas the α-CH_3 group of ketone reacted selectively over the CH_3 group in methyl ether (**4n**). Only slight selectivity was observed between the methyl group on aromatic rings and that in methyl ether (**4o**). The reasons for the selectivity between two types of α-C−H in **4m** as well as the lack of selectivity between two methyls in **4o** need to be further explored. Dichloromethane can also participate in the reaction as a representative of halogenated alkanes, affording the desired product in good yield (**4p**). It is noteworthy that the implantation of ether- (**4e**−**g**), acetal- (**4h** and **4i**), and ketone-containing groups (**4j**−**n**) into the spiro[5.5]trienones enables a handle for further structural modifications.

Several control experiments were conducted to gain an understanding of the mechanistic details, and trapping of the radical, the isotopic effect, and the source of the oxygen atom in the product were confirmed, as illustrated in Scheme 4. The dearomative cyclization did not take place in the absence of the benzyl radical source (**2a**), whereas the radical was successfully trapped by TEMPO and 1,1-diphenylethylene in the reaction between **1a** and **2a** under the standard conditions (Scheme 4a,b). These facts clearly indicated that radical intermediates derived from the C−H radical precursor were involved in the reaction. Meanwhile, a significant isotopic effect (**3a**/**3a-D**$_7$ 7:3) was observed when a mixture of equal equivalents of toluene (**2a**) and D_8-toluene (**2a-D**$_8$) was used to react with **1a** under the standard reaction conditions (Scheme 4c),

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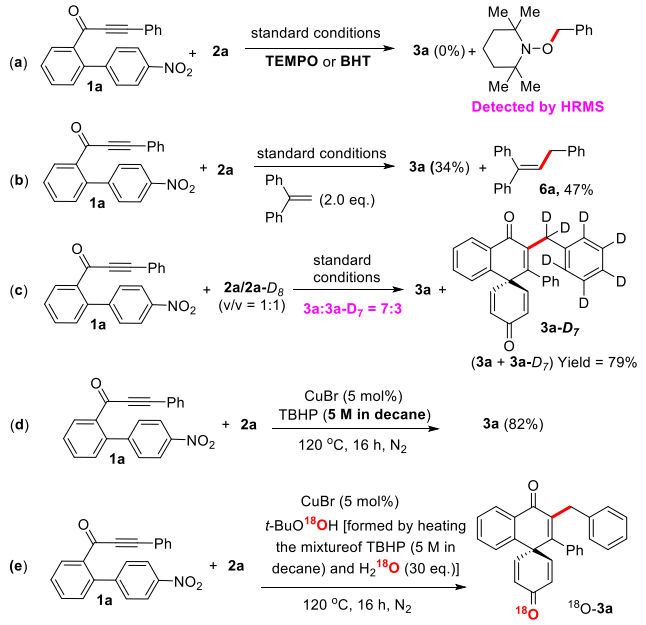
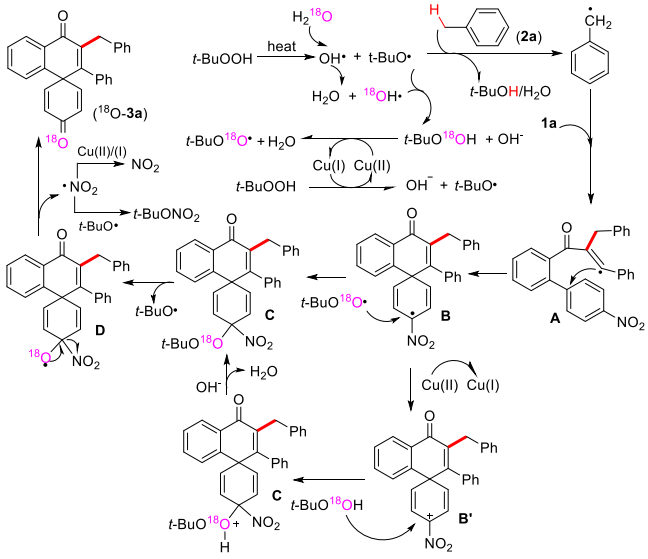
Scheme 4. Control Experiments



Scheme 5. Possible Mechanism



suggesting that the formation of the benzyl radical *via* the cleavage of C(sp^3)−H of toluene might be involved in the rate-determining step. To figure out how the nitro group left, we then determined the source of the oxygen atom of the carbonyl in **3a** formed by the cleavage of the nitro group. Because this reaction can proceed smoothly under anhydrous conditions to afford **3a** in a comparable yield (Scheme 4d), the oxygen in the newly formed carbonyl group should not come primarily from water. An ^{18}O-labeling experiment using *t*-BuO^{18}OH formed by heating the mixture of *t*-BuOOH (anhydrous, 5 M in decane) and $H_2{}^{18}O$ afforded the ^{18}O-labeled product (Scheme 4e; for details, see the Supporting Information), which clearly showed the source of oxygen in the newly formed carbonyl group. It should be mentioned that the exchange reaction producing *t*-BuO^{18}OH (*t*-BuOOH + $H_2{}^{18}O$ = *t*-BuO^{18}OH + H_2O) has been reported[13,21] and confirmed by us. (For details, see the Supporting Information.)

On the basis of the previously described study, we proposed a reasonable mechanism for this transformation (Scheme 5).[13,21] The reaction was supposed to start with the O−O homolytic cleavage of TBHP, which generated HO· and *t*-BuO· radicals. The *t*-BuO· abstracted hydrogen from **2a** to afford the benzyl radical, which subsequently added to the triple bond of **1a** to form the vinyl radical **A**. This radical underwent a 6-exo-trig cyclization to afford the radical intermediate **B**. The *t*-BuOO· or *t*-BuO^{18}O· coupled to radical intermediate **B** to furnish intermediate **C**. Alternatively, intermediate **B** was oxidized to carbocation **B′**, which reacted with *t*-BuOOH or *t*-BuO^{18}OH and subsequently afforded intermediate **C** after releasing a proton. Through the O−O or O−^{18}O homolysis, intermediate **C** formed **D**, which yielded **3a** or ^{18}O-**3a** via a denitration. The ·NO_2 released during denitration might be oxidized to NO_2 or couple to *t*-BuO· to form *t*-BuONO_2. It can be seen in Scheme 5 that the Cu ion could promote the formation of *t*-BuOO·, *t*-BuO·, carbocation **B′**, and NO_2 and thus played a catalytic role in the whole reaction.

In conclusion, we developed a novel and simple akylative/denitrative dearomatization using simple catalyst and aqueous TBHP with readily available alkylating reagents, which afforded diversified alkylated spiro[5.5]trienones in good yields. Whereas dearomative 5-exo-trig cyclizations to spiro[4.5]-trienones have been extensively achieved,[13,22] the corresponding 6-exo-trig cyclizations furnishing spiro[5.5]trienones have rarely been reported.[14c,12,23] Moreover, the radical-type dearomative cyclization of biaryl ynone to spiro[5.5]trienones has only successfully achieved difluoromethylation, sulfonylation, and phosphorylation in the literature.[12] Thus our transformation provided the first examples of a general alkylative dearomatization to spiro[5.5]trienones. In addition, the reported dearomatization relied on a MeO of biaryl ynone to form the C═O group in the products via demethylation. For the first time, we have accessed spiro[5.5]trienones through an alkylative spirocyclization by using an unactivated aryl nitro as a leaving group. In sharp contrast with the previous activation of nitro groups, which mainly involved the ipso substitution of a nitro group, our protocol provides a unique strategy for the activation of nitro groups, for it involves not only a nitro's ipso substitution but also alkylation/alkenylation at other positions. Thus we expect that these findings will provide implications for the activation of aryl nitros and the development of related new reactions.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c00469.

Experimental procedures, characterization data, and NMR spectra for products (PDF)

Accession Codes

CCDC 1901346 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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